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A Physicochemical Study of Sugar Palm (*Arenga Pinnata*) Starch Films Plasticized by Glycerol and Sorbitol

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Abstract. The present work explores the physicochemical characteristics of sugar palm starch film for a potential hard capsule purpose. Sugar palm (*Arenga pinnata*) starch films were plasticized with glycerol or sorbitol in various concentrations (30% up to 50% w/w starch). Their effects on physicochemical properties of the films were investigated. The results showed that sugar palm starch was successfully developed as the main material of film using casting method. Incorporation of both glycerol or sorbitol affected the properties of films in different ways. It was found that thickness and solubility increased as plasticizer concentration increased, whereas retraction ratio, swelling degree and swelling thickness decreased with the increased plasticizer concentration.

INTRODUCTION

Capsule is very popular among the oral drug delivery systems mainly because it is easy to be swallowed. For decades, gelatin has been chosen as the main material of capsule production because of its excellent characteristics including gelling and film forming. However, there are some serious disadvantages of gelatin capsule including moisture instability to hygroscopic drugs and the surrounding humidity, limited acceptability due to religious restriction; and safety doubts since gelatin is mainly made from animal skin and bones.

Within the last several decades, there has been an increasing interest among researchers to find a new material with unique functional properties as gelatin. Numerous studies have been conducted to explore and develop various materials to replace gelatin in capsule shell production. Many researchers have investigated and developed natural substances from vegetal sources into medical capsule material. Numerous natural polysaccharides have also been investigated for their potentials to replace gelatin [1-3].

Among natural polysaccharides, starch has attracted an enormous attention due to its relatively low prices, abundant availability[4-6] and film-forming properties [7-10]. Many studies have been reported on starch-based film with various casting method. Although starch has inferior property in moisture barrier due to its hydrophilic nature, starch-based films are reported to have good oxygen, carbon dioxide and lipid barrier properties [11]. In its native form, starch film is brittle; thus, plasticizers are commonly incorporated to overcome film brittleness and increase film flexibility by increasing the intermolecular spacing [12]. In general, polyols are commonly added as plasticizers in starch-based films.

In spite of the fact that Indonesia is one of the promising sugar palm starch producers, many studies on sugar palm starch film were reported [13-15]. However, similar to sago starch, there is few studies on the use of sugar palm starch for pharmaceutical purpose, especially as a gelatin replacer for capsule shell production. Sugar palm starch is a promising material to replace gelatin since it contains ± 29% amylose [16]; thus, it has a good film forming capacity.

While the majority of previous studies developed the sugar palm starch film with starch concentrations less than 9% w/w [13-15], the present study developed film formula with high content of sugar palm starch. In terms of capsule shell production through the dipping method, a film formula with appropriate viscosity must be provided, so that it can form gel on the surface of the pins. Additionally, there is limited information on the effect of plasticizer on starch film properties prepared with high concentration of starch. Therefore, in the present study the effects of high content of starch in combination of various glycerol and sorbitol concentration were investigated. Several film formulas were developed during the study. Physicochemical properties of these formulas, such as appearance,

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thickness, retraction ratio, moisture content, solubility in water, swelling degree and swelling thickness were studied. A study of physicochemical properties of film is required in order to provide basic information for an appropriate application of the resulted film. In the future, one formula with the most suitable character for hard capsule, including mechanical and barrier properties of the film, will be selected for further film development.

EXPERIMENTAL WORK

Materials

Native sugar palm (*Arenga pinnata*) starch was obtained from PT. Aren Mulya, a sugar palm starch industry in Klaten, Central Java, Indonesia. Starch was washed and dried overnight at 40°C. Dried starch was crushed, ground and sieved. This material was used throughout the research to obtain reproducibility and consistent results. Chemical composition of sugar palm starch was determined according to the AOAC technique [17]. Other reagents including glycerol, sorbitol and Magnesium nitrate/$Mg(NO_3)_2$ were analytical grade.

Film-Forming Solution Preparation

Nine different film solutions based on plasticizer were prepared and processed into films using casting method. A method by Bae et al. [3] was adopted with some modifications. An amount of glycerol or sorbitol (30, 35, 40, 45 and 50% w/w starch) was dispersed in water and maintained under continuous agitation at 50°C for 30 min. Native sugar palm starch (9% w/v) was added to the aqueous glycerol or sorbitol dispersion. Film without plasticizer was used as a control. All film solutions were heated gradually from 50°C to 90°C under constant stirring and maintained at 90°C for 30 min. The film solutions were degassed under vacuum in order to remove the dissolved air. The resulted homogeneous and clear film solutions were poured onto an acrylic plate fitted with rims around the edge then dried overnight at 50°C. The films were peeled carefully, cut into test specimens, stored in a desiccator under 52% RH at 25°C for at least 48 h before analysis.

Physicochemical Characterization of Films

Film thickness was measured using a micrometer (Mitutoyo, Japan). The thickness of film was assessed at ± 25°C and expressed as an average of nine random measurements. The measurements were conducted ten replications.

The film retraction ratio was determined according to The et al. [8] and determined using the following formula:

$$Retraction\ ratio\ (\%) = \frac{initial\ film\ thickness - dried\ film\ thickness}{initial\ film\ thickness}\ x\ 100\% \quad (1)$$

The moisture content of the starch film and the starch-plasticizer film samples was determined gravimetrically by drying the samples at 105°C for 24 h [17]. The moisture content was calculated as the percentage of water removed from the initial mass sample. All experiments were carried out in ten replications.

The swelling behavior of sugar palm starch film was determined by measuring the weight change of film upon soaking in distilled water at room temperature. Changes in weight were monitored for a different period. The wet weight of the film was determined by first blotting the surface of films with filter paper to remove excess water and the film weighed immediately. Ten replications were performed to obtain and average value. The percentage of swelling degree and swelling thickness were calculated as follows:

$$Swelling\ degree\ (\%) = \frac{weight\ of\ final\ sample - weight\ of\ initial\ sample}{weight\ of\ initial\ sample}\ x\ 100\% \quad (2)$$

$$Swelling\ thickness\ (\%) = \frac{final\ thickness - initial\ thickness}{initial\ thickness}\ x\ 100\% \quad (3)$$

In order to determine the solubility of films in water, a method by Shih [18] was adopted with slight modification. Film samples of 20 mm x 20 mm were prepared, weighed and immersed in 25 ml distilled water. The samples were under mild agitation at 175 rpm using an orbital incubator at 37°C for 1 h. The remained pieces of film were collected by filtration and dried again. The dry mass content of initial and final films was determined by drying the sample at 105°C for 24 h. The solubility of films was calculated by following formula:

$$Solubility\ (\%) = \frac{initial\ dry\ weight - final\ dry\ weight}{initial\ dry\ weight}\ x\ 100\% \quad (4)$$

RESULTS AND DISCUSSION

The chemical composition of sugar palm starch is moisture (10.27%), ash (0.25%), crude nitrogen (0.42%), crude fat (0.03%). The amylose content of sugar palm starch, which is 33.37%, is in line with the result of other investigations [16, 19-20]. This amylose content indicates that sugar palm starch is suitable for film formation.

It is important to prepare film solution with proper concentration. Based on the preliminary study, it is hard to obtain tough capsule shell when the starch concentration is less than 9% w/w. Meanwhile, when the starch concentration is higher than 9%, the solution is too viscous; so that it is hard to produce smooth capsule shell. Therefore, the present study uses starch concentration of 9% w/w. In general, plasticizers are primarily added to improve the flexibility of films. The content of plasticizer may vary (20 – 60% w/w polymer), depending on the plasticizer and the desired properties of films. According to Sanyang et al. [15] who successfully developed sugar palm starch film with plasticizer content of 30%, the present investigation develops film formula with the minimum plasticizer concentration of 30%. Meanwhile, the maximum plasticizer concentration of 45% w/w starch for glycerol and 50% w/w starch for sorbitol is chosen based on the report of Poeloengasih and Anggraeni [21].

In the present work, all plasticized films are homogeneous, translucent with smooth surface and able to be peeled from the casting plates without tearing. On the contrary, unplasticized film is very brittle and cracked upon drying. Both glycerol and sorbitol are compatible with the starch matrix; hence it produces films with good flexibility. However, it is unexpected that at a relatively low plasticizer concentration (30% w/w starch), the sorbitol-plasticized film is intact but quite brittle with some cracks on the edge, so that it is difficult to handle. Meanwhile, at a relatively high glycerol concentration (50% w/w starch), the film is too sticky and hard to detach from the plates. These results show that both plasticizer affect the properties of films in different ways. Therefore, film with sorbitol content of 30% and glycerol content of 50% are not analyzed due to the difficulty in handling.

The average thickness and retraction ratio of plasticized and unplasticized film after being subjected at 25°C for at least 2 days under 52% RH varied as shown in Table 1. Unplasticized films with 0.111 mm of thickness is the thinnest, whereas with the addition of plasticizer, the thickness of films varied from 0.120 to 0.141 mm and from 0.113 to 0.150 mm for glycerol and sorbitol, respectively. Furthermore, changes in film thickness are observed with the addition of higher concentration of plasticizer. Incorporation of greater amount of plasticizer increases the total soluble matter of solution, so that it increases film thickness.This result is in line with Mali [4]. With increasing solid concentration in the film solution, the films become thicker.

TABLE 1. Comparison of thickness, retraction ratio and moisture content of sugar palm starch films plasticized with gycerol and sorbitol

Type of plasticizer	Concentration of plasticizer (%)	Thickness (mm)	Retraction ratio (%)	Moisture content (%)
Control	0	0.111	94.43	15.6394
Glycerol	30	0.120	94.00	16.9020
	35	0.129	93.55	21.3172
	40	0.136	93.20	26.5930
	45	0.141	92.95	33.3440
Sorbitol	35	0.113	94.35	8.7374
	40	0.125	93.75	8.3042
	45	0.134	93.30	8.1323
	50	0.150	92.50	7.961

The thickness of film is not only affected by the solvent reduction during drying and soluble matter content in film solution, but also by retraction phenomenon that usually occured in film casting technique. It has been reported that concentration of dry matter of film solution and shrinkage during drying control film thickness [8]. Meanwhile, shrinkage of film throughout the drying stage is strongly affected by the initial casting thickness, since it determines the drying period. In the present research, the volume of spreading film solution is constant. As a consequence, each formula has the same initial casting thickness. In the present work, unplasticized film has the highest retraction ratio, i.e. 94.43%, whereas the glycerol- and sorbitol-plasticized films have a similar retraction ratio ranged from 92.95 to 94% and from 92.5 to 94.35%, respectively. However, at the same concentration, the addition of sorbitol is found to have a slightly higher retraction ratio value.

The moisture content of plasticized and unplasticized films after being conditioned under 52% RH at 25°C for at least 48 h is presented in Table 1. It is confirmed that the moisture content of glycerol-plasticized films is higher than that of sorbitol-plasticized films and control. It is also found that the moisture content of films plasticized with glycerol increases as the glycerol content increased. This is due to the fact that glycerol is a hygroscopic material and also a good water holding agent. As a consequence, it would increase the water content of films as well as perform as a plasticizer.

On the contrary, addition of sorbitol produces films with low moisture content, even lower than control, and there is a slightly decreasing tendency in the moisture content as sorbitol concentration increased. Glycerol and sorbitol are polyols and have similar straight-chain molecule. Both have different molecular weight, *i.e.* 92.09 g/mol for glycerol and 182.17 g/mol for sorbitol, and hydroxyl group content. Because sorbitol contains more hydroxyl groups than glycerol and owns similar molecular structure of glucose, it has a higher opportunity to react with starch chain, thus offers higher intermolecular forces. As a result, less hydroxyl groups are available to interact with water. Consequently, the sorbitol-plasticized films has lower moisture content than the glycerol containing films. These results are in line with the previous study by Godbillot et al. [22] that film composition would affect its moisture content.

Swelling degree and swelling thickness of sugar palm starch films after being stored at 25°C for at least 2 days under 52% RH is evaluated and are presented in Table 2. In general, all films keep their integrity after 60 min of water immersion, even after 24 h (data are not shown). Opaque appearance is observed after 30 min of water immersion. All films absorb water in a faster manner during the early stage of immersion and less amount of water is/was absorbed as time increased. The results reveal that unplasticized film possesses the highest swelling degree as well as swelling thickness compared to other films throughout the observation. Meanwhile, glycerol plasticizing films display higher swelling degree and swelling thickness than sorbitol-plasticized films. An increase in plasticizer content lead to a decrease in swelling degree and swelling thickness for both plasticized films.

TABLE 2. Comparison of swelling degree in various times, swelling thickness and solubility in water of sugar palm starch films plasticized with gycerol and sorbitol

Type of plasticizer	Concentration of plasticizer (%)	Swelling degree (%)		Swelling thickness (%)	Solubility in water (%)
		30 min	60 min		
Control	0	177.6430	187.9285	153.0908	3.6782
Glycerol	30	140.3922	149.4183	97.3407	22.1865
	35	130.0299	135.8684	97.0397	24.1975
	40	104.9746	109.3075	81.3273	26.7769
	45	80.7029	81.8075	69.2518	28.2252
Sorbitol	35	101.5349	105.2003	93.6135	31.5626
	40	93.9530	98.4688	86.1690	33.2439
	45	88.7400	90.9732	82.4197	34.7176
	50	78.1506	79.8473	66.1618	37.0503

According to Chen et al. [23], high swelling degree is due to high amylopectin and low amylose content. In other words, swelling degree is affected by starch (type, concentration, amylose/amylopectin ratio, etc.) and its interaction in the film matrix. Without the addition of plasticizer into the film solution, there is only starch–starch interaction in the film matrix, whereas by the incorporation of plasticizer, interaction in film matrix vary, *i.e.* starch–starch, starch–plasticizer and plasticizer–plasticizer. Hence, when the unplasticized film is/was immersed in water, the chance of water to interact with starch is higher since there is no plasticizer that could avoid the interaction between water and starch. Therefore, unplasticized film possesses the highest swelling degree and swelling thickness since there is intensive interaction between starch and water. It is observed that the swelling degree and swelling thickness of unplasticized film after water immersion for an hour were 187.9285% and 153.0908%, respectively.

On the other hand, film swelling degree and swelling thickness decrease with the plasticizer addition (Table 2). It is also found that the swelling degree and swelling thickness decrease as the plasticizer concentration increases. At high plasticizer concentration, the chances of starch interacting with water molecules become lesser. It is visible that the swelling degree of glycerol-plasticized sugar palm starch films after 30 min of water immersion range between 80.7029% and 140.3922%, whereas the swelling degree of sorbitol containing films range from 78.1506% to 101.5349%. Among the samples, the film with 45% (w/w starch) of glycerol and 50% (w/w starch) of sorbitol show the lowest value of swelling degree and swelling thickness.

The solubility of film in water is an important property of film. It shows integrity and resistance of film in water and consequently determines the application of film. In terms of the production of capsule shells, an appropriate film formula for hard capsule must be provided and its characteristics must be identified. including solubility. Generally, when the concentration of plasticizer increases, the solubility of the films will increase [24].

The results of the measurement of film solubility show that the film solubility increases with the addition of plasticizer. After being immersed in water, unplasticized film display minor solubility (approximately 3.6782%), whereas plasticized films present solubility that varied from 22.1865 to 28.2252% for glycerol and from 31.5626 to 37.0503% for sorbitol (Table 2). Changes on water solubility are noticed with the addition of higher content of plasticizer. There is an increasing tendency of water solubility when plasticizer concentration increases. This is due to the hydrophilic character of plasticizers. This is in agreement with other studies that solubility of starch films increases with higher plasticizer concentration [25, 26].

CONCLUSIONS

Sugar palm starch is successfully developed as the main material using casting method for the preparation of films. Addition of glycerol and sorbitol in various concentrations could effectively improve the physicochemical properties of films and affect the properties of films in different ways. In conclusion, the characteristic of films, such as thickness and solubility in water increase with the increases in plasticizer concentration. Meanwhile, there is a decreasing tendency of retraction ratio, swelling degree and swelling thickness as plasticizer concentration increased. In order to provide a general overview of the films' characteristics, further investigation on mechanical and barrier properties of sugar palm starch films is important to be carried on, so that a film formula with the most suitable characteristics for hard capsule could be selected and developed.

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